Microstructure Evolution of Poly[tetrafluoroethylene-co-(perfluoropropylvinylether)] Films Under Uniaxial Deformation

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Abstract

This paper presents an investigation of semi-crystalline poly[tetrafluoroethylene -co-(perfluoropropylvinylether)] (PFA) films uniaxially drawn at two temperatures. The extent of crystal unit cell orientation increased significantly with drawing at both draw temperatures as expected, but crystallinity was found to increase with draw ratio only at the lower draw temperature, remaining unchanged at the higher temperature. Considering the evolution of small-angle X-ray scattering patterns as a function of deformation, a model for the changes in PFA lamellar microstructure on drawing was developed. The observed mechanical α and γ relaxations of PFA were assigned to relaxation of rigid and mobile amorphous segments, respectively. Drawing at 200 °C to a draw ratio of 7 leads to a ~40 °C increase in the α transition temperature compared to the unoriented film, and the findings support the key role of molecular orientation in suppressing the cooperative motions of non-crystalline segments in drawn polymers.

Introduction

Poly[tetrafluoroethylene-*co*-(perfluoropropylvinylether)] (PFA), a random copolymer consisting primarily of tetrafluoroethylene units, is well known to exhibit a variety of desirable properties (e.g. excellent chemical resistance and low coefficient of friction) [1-3] and as a result it has been used in a variety of applications including in the area of optical materials [4, 5]. PFA also has an advantage over the widely-used polytetrafluoroethylene (PTFE) homopolymer as it is much easier to process, and can be manufactured into high quality thin films, extending its applications. It exhibits excellent, relatively temperature insensitive, dielectric properties (e.g. high volume and surface resistivity) [6-8] and is therefore suitable for applications such as insulation of communication cables or components for electronic devices where low electrical energy dissipation is necessary at high frequencies [9, 10].

Although PFA has some advantages over PTFE, there have only been limited systematic microstructural studies on semi-crystalline PFA and related TFE (tetrafluoroethylene) - fluoroether copolymers, and very few on structural changes on mechanical deformation [1, 11, 12]. Fujimori and Hayasaka [1] have proposed that poly[tetrafluoroethylene-*co*-(perfluoroethylvinylether)] (EFA) drawn fibers form oriented lamellar crystal stacks at lower strains, which transform into a tilted lamellar arrangement (herringbone-like) upon further drawing.

The aim of the present work is to investigate in detail the effect of uniaxial deformation on crystalline microstructure and dynamics of PFA films. Both wide- and small-angle X-ray scattering measurements were employed to characterize the microstructural evolution of PFA films on drawing, augmented by differential scanning calorimetry to determine degrees of crystallinity. Chain dynamics were studied using dynamic mechanical analysis at a fixed frequency over a broad temperature range.

Experimental Section

Materials

Poly[tetrafluoroethylene-*co*-(perfluoropropylvinylether)] films (Chemours Teflon™ PFA) were purchased from American Durafilm. PFA is a random copolymer obtained from the polymerization of TFE ($-\text{CF}_2-\text{CF}_2-$) and a perfluoropropylvinylether comonomer ($-\text{CF}_2-\text{CF}(\text{OCF}_2\text{CF}_2\text{CF}_3)-$). The comonomer content in PFA has been reported to be approximately 7 wt% [1]. The thickness of the as-received PFA film was $\sim 250\text{ }\mu\text{m}$.

Drawing of PFA films

PFA films were drawn uniaxially using an Instron Model 5866 in an air oven at 140 and 200 °C. Films were first exposed to 140 °C for 5 min before stretching, ensuring the evenness of temperature in the cabinet and samples, and the extension rate was fixed at 10 mm/min. Separate samples were elongated to 100%, 150%, 200%, 300% and 400%, and then held at 140 °C until the load became approximately constant. Samples drawn at 200 °C to 200% and 600% extension were prepared in the same fashion.

Characterization

Small-angle X-ray scattering (SAXS) experiments were used to explore crystal lamellae microstructure and orientation. SAXS data were collected using a Molecular Metrology instrument with a Cu K α radiation source ($\lambda = 0.154\text{ nm}$) at 45 kV and 66 mA, using a two-dimensional multiwire detector with a sample-to-detector distance of 1.5 m. Wide-angle X-ray diffraction (WAXD) patterns were measured on a Rigaku Microfocus Micromax 007HF in transmission mode, using a Molybdenum point-focused source ($\lambda = 0.071\text{ nm}$). Typical image acquisition time was 20 s. The diffraction patterns were analyzed using the software GADDS.

Melting temperatures and degrees of crystallinity were determined by differential scanning calorimetry (DSC) using a TA DSC Q10 at a heating rate of 10 °C/min. Sample sizes of 5-7 mg were used, with temperature ramping from 25 to 350 °C. Dynamic mechanical analysis (DMA) of PFA films were performed on a TA instrument Q800 in air at a heating rate of 5 °C/min under strain-control in the temperature range of -150 to 200 °C. It should be noted that the tensile-

deformed samples used for DMA measurements were cut parallel to the extension direction, and fixed by two clamps in the deformation direction. The frequency of the deformation was 1 Hz for each sample.

Results and Discussion

Stress-Strain Behavior

A representative stress-strain curve for the initially undrawn PFA film at 140 °C is shown in Figure 1. It displays an initial linear region (primarily elastic deformation), followed by yielding, a longer plateau region, and an upturn in engineering stress beginning at an extension of ~250%. These are identified as Regions I, II, III and IV, respectively. The seven points marked on the curve represent the strains at which the microstructural, DSC and DMA measurements were carried out: i.e., draw ratios $\lambda = 1.0, 1.4, 2.0, 2.5, 3.0, 4.0$ and 5.0 .

Figure 1. Representative engineering stress-strain curve of PFA films at 140 °C. The symbols along the curve indicate the strains at which X-ray scattering, DSC and dynamic mechanical measurements were performed.

Melting Behavior

DSC thermograms of films at selected draw ratios at 140 °C and 200 °C are shown in Figure 2, and the corresponding melting parameters are collected in Table 1. The enthalpies of fusion (ΔH_m) gradually increase with draw ratio when drawing was conducted at 140 °C. Since the side

groups on the perfluoropropylvinylether comonomer units are undoubtedly rejected from the PTFE unit cell, the degrees of crystallinity were estimated using the perfect crystal heat of fusion of PTFE (82 J/g) [12, 13].

Figure 2. DSC curves of PFA films drawn at 140 °C (A) and 200 °C (B) to various draw ratios.

On drawing at 140 °C, the crystallinity increases progressively from 29% to 40%, while no apparent change in melting point (T_m) was observed with increasing draw ratio. T_m s for selected films drawn at 200 °C, as well as the heats of fusion, are similar to that of the as received film. The latter behavior likely arises from competition between chain relaxation rate and strain induced crystallization [14]. Chain relaxation is faster at the higher draw temperature leading to less strain

induced crystallization at an equivalent strain rate.

Table 1. T_m , ΔH_m and crystallization degree of PFA films under various draw ratios from DSC.

Draw ratio: λ	At 140 °C							At 200 °C	
	1.0	1.4	2.0	2.5	3.0	4.0	5.0	3.0	7.0
T_m (°C)	308	308	308	308	309	309	309	307	306
ΔH_m (J/g)	24	25	25	25	26	32	33	25	25
Crystallinity (%)	29	30	30	31	32	39	40	30	30

Drawing-induced Molecular Orientation

2D WAXD patterns for the undrawn and drawn PFA films are displayed in Figure 3. The as-received PFA film exhibits two readily apparent isotropic diffraction rings, indicating a lack of unit cell orientation. As draw ratio increases, the diffraction intensity of the inner ring becomes concentrated along the equatorial direction (which becomes sharper and stronger as draw ratio increases) and the outer diffraction ring becomes centralized along the meridian.

Figure 3. 2D WAXD patterns of PFA films at various draw ratios at 140 °C.

Figure 4 shows the 1D WAXD profiles of PFA samples integrated along the equator, where q is the scattering vector ($q = (4\pi \sin\theta) / \lambda$; θ is the Bragg angle). The sharpest and strongest reflection (corresponding to the inner ring in Figure 3) is located at $q = 12.8 \text{ nm}^{-1}$, which has been assigned for a similar EFA copolymer to the (110) reflection of an orthorhombic unit cell structure [1]. There is a shoulder at $q \approx 12 \text{ nm}^{-1}$ for the undrawn PFA film, which has been identified with the amorphous halo in EFA, and is progressively masked by the (110) intensity due to strain-induced crystallization on drawing. An additional WAXD reflection is observed at $q = 6.5 \text{ nm}^{-1}$, as shown in Figure 4B. Few reports have confirmed the presence of this small peak, except for Fujimori et al. [1, 11] who assigned it to the (100) reflection in an orthorhombic system. This peak shifts to lower q with increasing draw ratio (≈ 6.5 to $\approx 6.25 \text{ nm}^{-1}$). From the viewpoint of one-dimensional profiles scanned along the equatorial direction, the peaks located at $q = 21.8, 25.0$ and 33.4 nm^{-1} can be ascribed to (120) , (220) and (420) crystal planes, respectively. This matches with the scattering pattern observed for PTFE [1], not surprising in that the PFA unit cell structure is composed of repeating tetrafluoroethylene units.

Figure 4. 1D WAXD patterns (along the equatorial direction) of PFA films drawn at 140 °C to various draw ratios.

As the diffraction peak at $q = 12.8 \text{ nm}^{-1}$ is the strongest and displays the greatest changes upon extension, we chose this reflection to evaluate the degree of orientation of the deformed films. As shown in Figure 5, the original PFA sample exhibits isotropic diffraction rings at $q = 12.8 \text{ nm}^{-1}$, giving rise to essentially no features in the azimuthally scanned one-dimensional WAXD profile. As the draw ratio increases, the diffraction intensity becomes concentrated along the equatorial direction, in keeping with progressive orientation of the crystalline chain axes along the deformation direction.

Figure 5. Azimuthal scans at $q = 12.8 \text{ nm}^{-1}$ for PFA films drawn at $140 \text{ }^{\circ}\text{C}$ to various draw ratios.

To obtain the extent of unit cell orientation, the Hermans' function [15-17] was used, based on the (110) plane (at $q = 12.8 \text{ nm}^{-1}$),

$$f_c \cdot 100\% = [3 \langle \cos^2 \phi_c \rangle - 1] / 2 \quad (1)$$

f_c is the orientation factor along the draw direction and ϕ_c is the azimuthal angle ($= 0$ at the equator and 90° at the meridian). The value of f_c would be equal to -0.5 for perfect alignment perpendicular to the draw direction, 0.0 for no alignment, and 1.0 for perfect alignment with the draw direction. The numerical values of the mean-square cosines in this equation can be determined from the corrected intensity distribution for this crystalline plane, $I_c(\phi_c)$, averaged over the entire surface of the orientation sphere:

$$\langle \cos^2 \phi_c \rangle = \frac{\int_0^{\pi/2} I(\phi_c) \cos^2 \phi_c \sin \phi_c d\phi_c}{\int_0^{\pi/2} I(\phi_c) \sin \phi_c d\phi_c} \quad (2)$$

Calculated f_c values for samples with various draw ratios are listed in Table 2 and increase from 0 to 0.86 , indicating very significant preferential orientation along the drawing direction. By way of comparison with other highly oriented fluoropolymers, poly(vinylidene fluoride) deformed uniaxially to a draw ratio of 9.0 reaches an f_c value as high as 0.99 [18].

Table 2. Calculated orientation factors of the prepared PFA films.

Draw ratio	1.0	1.4	2.0	2.5	3.0	4.0	5.0
Orientation factor	0	0.21	0.50	0.66	0.74	0.84	0.86

Figure 6. 2D WAXD patterns of PFA films drawn at 140 and 200 °C.

To investigate the influence of draw temperature on PFA crystalline orientation, WAXD patterns of selected samples drawn at 200 °C were also obtained. Figure 6 compares the 2D WAXD profiles of PFA films drawn at 140 and 200 °C. Elevated temperature drawing does not lead to any significant difference in crystalline orientation for a draw ratio of 3.0; the calculated degree of orientation using the (*110*) reflection is essentially the same for each (0.74 and 0.75, for 140 and 200 °C, respectively). However, the ultimate draw ratio is significantly improved at elevated temperature, with the maximum achievable draw ratio in our experiments ~ 7.0 at 200 °C vs. 5.0 at 140 °C. An important change occurs for the WAXD pattern at a draw ratio of 7.0 in the meridional direction, indicative of a better-defined ordered microstructure, where the arc in the outer ring splits into two sharp reflections. Based on the literature [1, 19], this relatively broad reflection is associated with the (*116*) plane in the orthorhombic unit cells. Although the degree of crystallinity is comparatively lower for PFA drawn to 7.0 at 200 °C vs. 5.0 at 140 °C, the extent of unit cell orientation is significantly higher (based on the diffraction peak at $q = 12.8 \text{ nm}^{-1}$), i.e., 0.92 compared to 0.86.

Drawing-induced lamellar rearrangement

Figure 7. 2D SAXS patterns for PFA films drawn at 140 °C to various draw ratios.

Figure 7 displays the 2D SAXS patterns for films drawn at 140 °C. For the as-received PFA film, an isotropic SAXS pattern is observed, indicating a randomly oriented lamellar texture. At draw ratios of 1.4 and 2.0 (i.e., in Region II of the stress-strain curve, Figure 1), the dark inner ring begins to split into two symmetric arcs located along the equatorial direction, similar to our recent findings on semi-crystalline poly(ethylene-tetrafluoroethylene) [20]. This scattering arises from crystal lamellae having their normals directed transverse to the draw direction. The relative lack of intensity along the meridional direction suggests that scattering contrast from lamellae having their chain axes aligned along the draw direction is significantly reduced. As amorphous segments between lamellae extend and orient along the draw direction, their density would be expected to increase somewhat, leading to a reduction in X-ray scattering contrast [17,21]. Such an effect has been observed on a number of occasions, and these regions have been often referred to as ‘oriented mesophases’.

In Region III, at draw ratios of 2.5 and 3.0, two new scattering arcs appear along the meridian, indicating the formation of periodic lamellar structures along the draw direction. In

addition, the dark inner arcs are modified into a four-point pattern. Similar behavior has been observed at intermediate strains on uniaxial drawing of other semi-crystalline polymers, and has been associated with intralamellar slip of lamellae oriented between the parallel and perpendicular directions of the drawing [22,23]. As deformation increases further (Region IV), the scattering intensity becomes increasingly concentrated along the meridian in a broad two point pattern, indicative of lamellae orientation with their chain axes parallel to the draw direction. The patterns are slightly bent (not a well defined 4 point pattern) indicative of some interlamellar and/or intralamellar slip [1]. The reflections along the equator become much weaker, with some intensity remaining at draw ratio of 5.0 at low q . Low q scattering at higher draw ratios has been observed for many uniaxially oriented semi-crystalline polymers and is associated with inter-microfibril scattering and/or scattering from microvoids [e.g. 21,24]. Here, microfibril formation may have arisen from residual fragments of lamellae originally oriented transverse to the draw direction, these becoming drawn into elongated strands.

Figure 8. 1D SAXS for PFA films deformed to selected draw ratios at 140 °C: (A) Along the meridional and (B) equatorial directions.

To further investigate how PFA lamellae rearrange during uniaxial deformation, 1D SAXS profiles were obtained along both meridional and equatorial directions (Figure 8). The long period of the undrawn sample is 32.2 nm, which is on the order of that reported for some other fluorinated polymers such as EFA, for which a long period of 27 nm has been reported [1]. Region II represents

the onset of PFA yielding (at draw ratios ≤ 2.0). As seen in Figure 8, the long period (L) along the meridian and equator increase and decrease, respectively, with increasing strain. Generally, chain segments in the amorphous region are oriented along the tensile axis as samples are stretched. The sample elongates in this direction, but shrinks in the direction perpendicular to the draw axis. Therefore, the long period parallel to the draw direction would be expected to increase, while that perpendicular to drawing should be reduced. Figure 8 confirms this: in Region II, the period increases from ~ 32 to 41 nm in the meridional direction, but decreases from ~ 32 nm to 29 nm in the equatorial direction. During this stage of the deformation process, the changes in long period are mainly attributed to the rearrangement of chain segments in the amorphous region.

In Regions III and IV the most prominent change along the draw direction is the appearance of a scattering peak centered at $L = 17.5$ nm, signifying that a lamellar texture with a much smaller long period is formed. Chain segments in the amorphous region became extended and can more readily crystallize into new crystals oriented along the stretching direction, similar to observations as reported by Kamal et al. [25], and this scattering feature likely arises from additional strain-induced crystallization between the original lamella. In the equatorial direction, no significant change in the long period was observed, but the scattering peaks become weaker with increasing strain, in keeping with progressive lamellar orientation along the draw axis.

Figure 9. 2D SAXS patterns of PFA films stretched at 140 (top row) and 200 °C (bottom row).

Figure 9 displays selected 2D SAXS patterns of PFA deformed at 140 and 200 °C. As differences in scattering after drawing at these two temperatures are not readily apparent in the 2D images, 1D SAXS profiles after drawing at 200 °C along both meridional and equatorial directions are shown in Figure 10. Broadly similar trends are observed for samples drawn at 200 °C compared to those drawn at 140 °C (Figure 8). The long period along the draw direction (meridian) at draw ratios of 3.0 and 7.0 (21.5 nm) is larger than those of the comparable films drawn at 140 °C (17.5 nm). It is possible that the extensive strain-induced crystallization at 140 °C caused some densification of the lamellar stacks, thus reducing the long period. This effect would be muted for films drawn at 200 °C, having far less strain crystallization (Table 1).

Similar to drawing at 140 °C, the scattering peak along the equator becomes much weaker with increasing strain, but a small second scattering maxima (the relative scattering intensity axis is on a log scale) appears at higher draws ratios at $q \sim 0.55 \text{ nm}^{-1}$ ($L \sim 11 \text{ nm}$). In fact, the scattering from lamellae in the unoriented film along the equator is relatively broad, and some scattering at higher q is essentially maintained on drawing, similar to the scattering along the meridian for the films drawn at 140 °C (Figure 8). This suggests that even at the highest draw ratios achievable in the present study a small fraction of lamellae remain with their normals transverse to the draw direction.

Figure 10. 1D SAXS for PFA films at various draw ratios deformed at 200 °C: (A) In the draw direction (along the meridian) and (B) In the equatorial direction.

Based on the evolution of the SAXS patterns, a simple schematic model for the changes in PFA lamellar microstructure on drawing is shown in Figure 11. In the initial yielding stage (Figure 1), drawing primarily influences the arrangements of chain segments in amorphous regions, leading to extension of the periodical structure along the draw axis but shrinkage perpendicular. In the plateau region, strain-induced crystallization occurs, giving rise to a modified lamellar structure oriented with respect to draw axis, while simultaneously the lamellae oriented at an angle to the draw direction gradually fragment and align with the draw direction, assembling into microfibrils. In the strain-hardening region, further extension leads to increasing lamellar orientation (with chain axes) parallel to the draw direction, presumably accompanied increasing lamellar fragmentation.

Figure 11. Schematic model of the microstructural evolution of PFA films on drawing, illustrating oriented mesophase formation and strain-induced crystallization.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) [26,27], and more recently dielectric relaxation spectroscopy (DRS) [16,28], have been used to investigate the effect of mechanical strain on polymer dynamics. In the present study, attempts were made to utilize DRS for characterizing the relaxation processes of unoriented and oriented PFA films. However, the dielectric loss ($\tan \delta$) of all samples from -100 - 200 °C is very low, $\leq 6 \times 10^{-4}$ in $\tan \delta$, which is below the lowest loss measureable by our current Novocontrol dielectric spectrometer.

The origin of the relaxation processes in semi-crystalline polymers is often not clear from the literature, due to the complex heterogeneous nature of the non-crystalline segment environment. An excellent example is PTFE (and its copolymers), with glass transition temperatures (T_g) reported using various experimental methods ranging from ~ -115 to 120 °C [29, 30]. Moreover, two distinct T_g s (or two dynamic segmental relaxations) have been reported for a number of semi-crystalline polymers, and these have been associated with segmental motions of a less constrained ‘mobile amorphous fraction’ (MAF) and a fraction whose motions are significantly constrained by their proximity to lamellar crystals (the so-called ‘rigid amorphous fraction, RAF’) [30-32].

Figure 12A and B display the storage moduli (E') and $\tan \delta$, respectively, as a function of temperature for the unoriented and drawn PFA films. Samples with draw ratios ≤ 2.0 exhibit three relaxation processes, designated herein as α , β and γ in order of decreasing temperature. The substantial decrease in E' at T_α for all samples signifies that this process is a dynamic segmental relaxation. The γ process is also accompanied by a very significant reduction in E' , which is rather atypical. Generally, γ and β processes are assigned to local processes and are characterized by rather weak relaxation strengths [33, 34]. In the present case however, both the reduction in E' and the intensity of the $\tan \delta$ peak for the γ relaxation are on the order of those for the α process. Therefore, we conclude that the γ process is not a local process but rather represents an additional, low temperature segmental relaxation process. Consequently we assign the α and γ transitions to segmental relaxation of rigid and mobile amorphous segments, respectively. Similar assignments have been proposed for these processes in the PTFE homopolymer by Calleja, et al. [30], and other

work has assigned a sub-zero temperature process in PTFE to segmental relaxation [35]. The intermediate temperature β process has been assigned to a crystal disordering transition for PFA and other PTFE copolymers [36]. It is interesting to note that the β relaxation is gradually suppressed as draw ratio increases.

As expected, for films drawn at 140 °C the storage modulus along the axis of deformation increases to some degree with increasing draw ratio at temperatures below T_{α} , in keeping with increasing chain orientation along the draw direction and progressively higher degrees of crystallinity. The dynamics of both the MAF and RAF segments are significantly slowed with increasing draw ratio and crystallinity; the γ process increases in temperature from -91 to -76 °C while the α relaxation shows an even larger dependence on draw ratio, increasing from 87 to 117 °C. The relative magnitude of the strengths of the α and γ processes is somewhat difficult to assess given the increasing breadth of the loss peak maxima with increasing draw ratio, but it can be seen generally (Figure 12B) that the magnitude of the α relaxation (associated with the rigid amorphous segments) decreases relative to the γ process with increasing draw ratio.

Figure 12. DMA data (1 Hz) for the unoriented PFA film and films drawn at 140 °C to different draw ratios: (A) storage modulus and (B) tan δ .

Figure 13. Dynamic mechanical loss ($\tan \gamma$) at 1 Hz for the unoriented PFA film and those drawn to the highest achievable draw ratio at 140 and 200 °C.

Finally, Figure 13 displays $\tan \delta$ data for PFA films stretched to the highest achievable draw ratio at 140 and 200 °C, along with the undrawn film. The β relaxation is strongly suppressed in the two highly drawn samples. Drawing at 200 °C has the same effect on T_γ (associated with the mobile amorphous fraction) as drawing at 140 °C, but the α process moves to a significantly higher temperature (129 °C) for the higher draw temperature / ratio due to further restriction in mobility of the rigid amorphous segments at the higher extension. In addition, even though the sample drawn 200 °C has a comparatively lower degree of crystallinity (the same as the undrawn film) the magnitudes of the α and γ processes decrease significantly compared to the other two samples in Figure 13. This indicates that rather than the crystallinity per se, the role of molecular orientation plays a key role in suppressing the cooperative motions of the non-crystalline segments in drawn films.

Summary

The microstructural evolution induced by uniaxial deformation of semi-crystalline PFA films was investigated using X-ray scattering, augmented by DSC measurements of the degree of crystallinity. Unit cell / lamellar orientation increases rather significantly on extension as expected: the WAXD Hermans' orientation factor reached 0.86 at the maximum draw ratio achievable on drawing at 140 °C. Drawing at 200 °C resulted in a maximum draw ratio of 7.0 and an orientation factor of 0.93. The degree of crystallinity was observed to increase with draw ratio at the 140 °C draw temperature (from 29 – 40%, arising from strain induced crystallization), but remained unchanged on drawing at 200 °C. We proposed that the latter finding arises from competition between chain relaxation rate and strain induced crystallization [14]. The initial unoriented films exhibited a stacked lamellar microstructure with a mean long period of ~32 nm, and transforms into a partially oriented microfibrillar morphology with smaller long period at higher draw ratios (see Figure 11).

The mechanical α and γ relaxations of PFA were assigned to relaxation of rigid and mobile amorphous segments, respectively. When drawing at 140 °C, the dynamics of both the mobile and rigid amorphous segments were significantly slowed with increasing draw ratio and crystallinity; the γ and α processes increased by 15 and 30 °C respectively at a draw ratio of 5.0. Although the crystallinity was the same as the undrawn film, drawing at 200 °C to a draw ratio of 7.0 lead to a ~40 °C increase in the α transition temperature and a reduction in intensity of the α and γ processes. These findings demonstrate the important role of molecular orientation in suppressing the cooperative motions of non-crystalline segments in drawn films.

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Graphical Abstract